

Investigation of the ν_8 and ν_{21} bands of propane $\text{CH}_3\text{CH}_2\text{CH}_3$ at 11.5 and 10.9 μm : evidence of large amplitude tunnelling effects.

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We present detailed investigations of the ν_8 band (C-C symmetric stretch at 870 cm^{-1}), an ν_{21} band (CH_3 rock at 921 cm^{-1}) of propane (C_3H_8). For both bands the rotational energy levels in the upper states are split because of interactions with the internal rotations of the methyl groups, leading to the identification of AA, EE, AE and EA torsional components. One of the results of the present study is to show that these torsional splittings are due to the existence of anharmonic and Coriolis resonances, coupling the 2^1 and 8^1 rotational levels to nearby highly excited levels of the two internal rotations of the methyl groups. An effective "vibration – torsion- rotation" Hamiltonian model was built in the G_{36} symmetry group which accounts for both types of resonances. In parallel, a code computing the line intensities was developed to allow unambiguous torsional component assignments. The line assignments were performed using a high resolution (0.0015 cm^{-1}) infrared spectrum of propane, recorded with synchrotron radiation at the SOLEIL French light source facility coupled to a Bruker IFS-125 Fourier transform spectrometer.

High resolution FTIR study of the ν_6 band of CH_2F_2 in 3 μm spectral region at low temperatures

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Difluoromethane belongs to the class of Freons, which are potential replacements for the ozone depleting 'chlorofluoro carbons' as refrigerants. Owing to its dense energy levels, it also serves as an ideal system for basic understandings on vibrational energy re-distributions. In this context, 3 μm region is particularly interesting as it contains fundamental (ν_1 and ν_6), combination ($\nu_2+\nu_8$) and overtone ($2\nu_2$ and $2\nu_8$) vibrations. The earlier studies carried out in this region [1-3] have highlighted the possibilities of couplings between various energy levels, which necessitates comprehensive studies of the rotationally resolved vibrational modes. Cooling of the gas sample is one of the effective methods in such cases, which can be used to decongest the spectrum and reduce the Doppler width. Consequently, a jet-cooled study of the ν_6 band (C-H asymmetric stretch, C-type band with origin at $\sim 3014.05046 \text{ cm}^{-1}$) had been carried out [4]. However, because of the introduction of extra cooling, the higher states were not populated and thus a total of only 286 transitions up to $J \leq 19$ and $K_a \leq 4$ could be assigned.

Hence, the present work is aimed at studying the transitions of ν_6 band involving high J and K values along with reduced Doppler width of spectral lines so as to obtain precise molecular constants. We have adopted a static cooling approach with a temperature of $\sim 160 \text{ K}$ estimated at the sample, which has drastically improved the spectral profile as compared to the room temperature spectrum, as shown in Figure 1 describing the ' Q_6 ' transitions. The spectra were recorded using an indigenous 26 cm long metallic cell using Bruker-IFS 125HR FTS instrument at an apodized resolution of 0.0025 cm^{-1} . Precise value for the band origin and centrifugal distortion constants up to 3rd order have been obtained by fitting ro-vibrational transitions upto $J \leq 50$ and $K_a \leq 14$ using Watson's A-reduced Hamiltonian in the I' representation. The details of various vibrational levels lying in this region and the possible coriolis interactions between them will be presented.

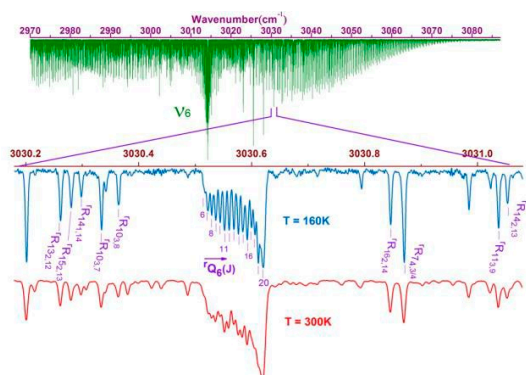


Figure 1: High resolution spectrum of ν_6 band of CH_2F_2 . The (lower) expanded view of ' Q_6 ' transitions at room temperature and 160K.

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The NH₂ scissors band of Methylamine

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Methylamine is a prototypical molecule with two large amplitude degrees of freedom: CH₃ internal rotation and NH₂ inversion which are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states.

For the first time a rotationally resolved spectrum of methylamine was recorded in the spectral region of the n_4 NH₂ scissors vibration using two infrared spectroscopic methods: a White-type multipass cell device (150 m optical path) coupled to the Bruker IFS 125 HR Fourier transform spectrometer implemented on the AILES beamline at the SOLEIL synchrotron facility, enabled to record a room temperature spectrum of the whole band in the 1540–1710 cm⁻¹ range at the maximal resolution of 0.001 cm⁻¹, and a quantum cascade laser spectrometer tunable around 6.2 μm coupled to a pulsed supersonic jet [1] (2.5 % CH₃NH₂ seeded in 5 bar neon) was used to record a low temperature high resolution spectrum in the 1622–1655 cm⁻¹ range of the n_4 R branch.

The goal of this work was to assign and analyze the NH₂ scissors band. The unresolved band contour of the NH₂ deformation of methylamine was observed around 1623 cm⁻¹ [2]. It is a hybrid band of A' symmetry in the C_s group (B₁ symmetry in the G₁₂ of PI group) with components of dipole moment change both parallel and perpendicular to the C–N bond. Using the LWW program adjusted for methylamine [<http://www.lww.amu.edu.pl>], it was possible to identify about 1000 transitions of B, E₁₊₁, E₁₋₁, and several lines of E₂₊₁ and A symmetry. The analysis of the NH₂ deformation IR band was supported by the laser spectrum: the rovibrational cooling of the supersonic expansion simplifies the congested rovibrational structure observed at room temperature, which makes easier to interpret sharp and well isolated lines. All assignments were confirmed with the GSCD. The attempt of global fit was made using a group theoretical formalism [3].

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Wrong distance – wrong line strength – wrong concentrations

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In the 60s D. Herriott, H. Kogelnik, and R. Kompfner published the concept of the so-called Herriott-cell. Two facing spherical mirrors build an optical multipass cell for long optical pathways, which are often used to measure low gas concentrations or the according absorption line parameters. This cell is used in various applications and its importance might become obvious from the fact, that this publication was cited more than 800 times.

Although it has been quoted so often, no one has apparently noticed a mistake in the formula for the distance 'd' of the Herriott-cell mirrors that is needed to realize a so-called closed configuration.

The formula is: $\cos(\theta) = 1 - (d/2f)$

In fact, the mirrors need to be placed slightly further apart. How much further depends on the individual configuration and was derived in the work presented here.

Based on this wrong formula for the mirror distances, J. Altmann, R. Baumgart, and C. Weitkamp calculated the optical path length for the multipath cells of the Herriott-type and published it in the 80s. Consequently, these theoretical path lengths are also deviating from the real ones. These wrong formulas have been used for the measurement of thousands of line intensities which can be found in various data bases.

Especially for complex models, like climate models, small changes in the parameters are leading to tremendous changes in the results. Accordingly, sub-percent uncertainties are targeted for line strength parameters and thus for gas concentrations measured via absorption spectroscopy. To realize these, the correct formula for the optical path length must be considered, because the deviations are typically of the same order of magnitude.

